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ELECTRICAL RELAXATION IN RARE EARTH DOPED CADMIUM
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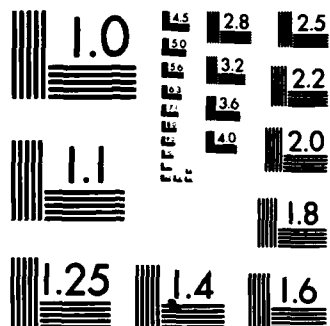
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Electrical Relaxation in Rare Earth Doped Cadmium Fluoride
by

John J. Fontanella & Mary C. Wintersgill

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<p>Audio frequency electrical relaxation measurements have been carried out over the temperature range 5.5 to 300K on CdF₂ doped with various concentrations of yttrium and eleven rare earths. Several relaxations are observed some of which are described in the present work. In contrast to rare earths in the alkaline earth and lead fluorides (and alkali metals in the alkaline earth, lead, and cadmium fluorides), no regularity is observed. However, three trends are suggested by the data, none of which is without exception. First, the samples exhibit very little relaxational behaviour for low concentrations. This implies that rare earths in cadmium fluoride, in general, do not form simple rare earth-fluorine interstitial pairs. Second, most of the relaxations occur for higher concentrations which suggests the presence of clusters. Finally, the room temperature electrical conductivity is relatively high</p>					
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(about 10^{-6} ohm-cm⁻¹) for most low concentration materials and tends to decrease with increasing concentration. This is consistent with the first two conclusions if at low concentrations rare earths are incorporated into the lattice in cubic sites and the conductivity is due to either to the non-local charge compensators or electrons. At high concentrations, then, the mobile charges either become trapped or their mobility is simply reduced by the clusters. This model agrees with the conclusions of Mho and Wright for CdF₂:Eu on the basis of site selective laser excitation studies. For CdF₂:Eu, a relaxation is found which correlates both with the B site of Mho and Wright and the principal ITC peak of Capelletti et al. This correlation sheds doubt on the assignment of the ITC peak.

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ELECTRICAL RELAXATION IN RARE EARTH DOPED CADMIUM FLUORIDE*

D. R. Figueroa

Universidad Simon Bolivar

Apartado 80659

Caracas, Venezuela

M. C. Wintersgill, J. J. Fontanella, D. A. Beam

Physics Department

U.S. Naval Academy

Annapolis, MD 21402, USA

C. G. Andeen

Physics Department

Case Western Reserve University

Cleveland, OH 44106, USA

ABSTRACT

Audio frequency electrical relaxation measurements have been carried out over the temperature range 5.5 to 300K on CdF_2 doped with various concentrations of yttrium and eleven rare earths. Several relaxations are observed some of which are described in the present work. In contrast to rare earths in the alkaline earth and lead fluorides (and alkali metals in the alkaline earth, lead, and cadmium fluorides), no regularity is observed. However, three trends are suggested by the data, none of which is without exception. First, the samples exhibit very little relaxational behaviour for low concentrations. This implies that rare earths in cadmium fluoride, in general, do not form simple rare earth-fluorine interstitial pairs. Second, most of the relaxations occur for higher concentrations which suggests the presence of clusters. Finally, the room temperature electrical conductivity is relatively high (about ~~10~~¹⁰⁰⁰⁰⁰ ohm/cm) for most low concentration materials and tends to decrease with increasing concentration. This is consistent with the first two conclusions if at low concentrations rare earths are incorporated into the lattice in cubic sites and the conductivity is due to either to the non-local charge compensators or electrons. At high concentrations, then, the mobile charges either become trapped or their mobility is simply reduced by the clusters. This model agrees with the conclusions of Mho and Wright for $\text{CdF}_2:\text{Eu}$ on the basis of site selective laser excitation studies. For $\text{CdF}_2:\text{Eu}$, a relaxation is found which correlates both with the B site of Mho and Wright and the principal ITC peak of Capelletti et al. This correlation sheds doubt on the assignment of the ITC peak.

INTRODUCTION

Cadmium fluoride will readily accept trivalent rare earth ions which take the place of Cd^{2+} ions and charge compensation is achieved by the incorporation of interstitial fluorine ions.^{1,2} However the question of whether for low impurity concentrations the F^- interstitials would be accommodated at nearest-neighbour or next-nearest-neighbour sites, as is the case for the alkaline earth fluorides, is still open. ESR and ENDOR measurements³ in $\text{CdF}_2:\text{Gd}^{3+}$ show that charge compensation does not occur within 7 Å of the Gd^{3+} ion. Optical spectroscopy studies⁴⁻⁶ of Eu^{3+} in CdF_2 reveal a multiplicity of sites, the most abundant being associated with non-local compensation of the Eu^{3+} by an F^- interstitial and with several types of clusters.

In contrast with the alkaline earth fluorides, there have been very few studies of the electrical relaxations associated with defect complexes in rare earth doped CdF_2 . ITC spectra of CdF_2 containing La^{3+} , In^{3+} and Gd^{3+} have been reported by Kunze and Muller⁷, but no signals due to dipolar reorientation were observed. Kessler⁸ reported a complex ITC spectrum containing several peaks for $\text{CdF}_2:\text{Y}^{3+}$ and two of them were attributed to dipolar reorientations. Capelletti et al^{9,10} found several peaks in the ITC spectrum for $\text{CdF}_2:\text{Eu}^{3+}$ which were a function of sample history and suggested the occurrence of some kind of precipitation of the simple dipoles. The present work reports the results of dielectric relaxation measurements on CdF_2 single crystals containing eleven rare earths and yttrium as dopants.

EXPERIMENTAL

All the cadmium fluoride crystals were supplied by Optovac, Inc. Slices about 1mm thick were sawn and polished before aluminum electrodes were evaporated onto the surfaces in a three terminal configuration. Complex impedance measurements were carried out using a fully-automated dielectric spectrometer operating at five frequencies from 10 to 10^5 Hz. In each case, the data were transformed to the complex dielectric constant using techniques described elsewhere.^{11,12}

RESULTS AND DISCUSSION

The dielectric relaxation spectra at 1000 Hz obtained during cooling from 300 to 5 K, for the as-received samples of CdF_2 doped with one of eight different rare earths, are shown in Figure 1. The data were taken at selected temperatures after the samples had been allowed to achieve thermal equilibrium. The spectra are arranged in order of decreasing ionic radii of the rare earth, and most correspond to relatively high impurity levels. Samples containing lower dopant concentrations in general showed very small or no dielectric relaxation signals. A similar behaviour was displayed by samples doped with other impurities such as Tb^{3+} and Ho^{3+} which are not shown in Figure 1. In some cases the spectra were obscured by severe noise which probably was caused by electron injection from the aluminum electrodes.

In comparing the spectra of Figure 1, there is no clear, consistent pattern. This is in contrast to the behaviour displayed by rare-earth doped alkaline earth fluorides and lead fluoride¹³ where regularity in the relaxation spectra with dopant ion size is always observed. Most of the

spectra for rare earth doped cadmium fluoride contain multiple relaxations and are quite complex. There is considerable overlap between several of the peaks which makes analysis of the data more difficult. Nevertheless, values for the parameters h and τ_0 in the Arrhenius equation:

$$\tau = \tau_0 \exp(h/kT) \quad (1)$$

were obtained for some of the peaks and these are summarized in Table I.

While there is no clear, consistent pattern, there are some common features for several spectra. For example, the three main peaks which were present for the samples doped with 0.01% Sm and 1% Ce can be described by similar fitting parameters. The intensities, however, are different. Cerium and samarium have similar ionic radii, and the observation mentioned above suggests that both impurities give rise to the same type of defect structure.

Next, a peak located at 163 K ($h=0.31$ eV) in the Ce and Sm doped samples, is also observed in the sample containing 0.001% Eu, as shown in curve (a) of Figure 2. The peak in the Eu doped sample is also described by similar fitting parameters, and these are close to those reported previously¹⁴ for CdF_2 doped with different amounts of sodium ($h=0.32$ eV and $\tau_0=1.62 \times 10^{-14}$ s). That peak was attributed to impurity $\text{Na}^+ - \text{F}^-$ vacancy dipoles. However, the maximum intensity of the peak in the Ce and Sm doped materials is much higher than for the peak observed in the 0.1% sodium doped material. Thus it is unlikely that the peaks in the trivalently doped crystals are due to inadvertent impurities present in either the starting CdF_2 powder or in the rare earth fluorides used for doping the

materials. The peak located at the lowest temperature (48.5 K) is stronger for the lower doping level in the samarium doped sample, but the opposite concentration dependence is observed for the intermediate temperature peaks. This would suggest a clustering mechanism involving simple rare earth- F^- interstitial pairs. However, the activation energy for reorientation of these dipoles (0.084 eV) is much smaller than the values found in the alkaline earth fluorides for simple rare earth-fluorine interstitial pairs. The several relaxations observed for other dopants in Figure 1, which are absent for lightly doped materials, also suggests the existence of a number of rare earth clusters of varying size and structure.

Figure 2 shows the dielectric spectra for as-received samples containing different nominal concentrations of europium (curves a to d). It is observed that only for the lightly doped sample (a) is a series of low intensity peaks observed in the low temperature region, the main component being at 163 K. As the doping level is increased to 0.1% Eu this peak structure disappears. Consequently, that peak is attributed to trace amounts of sodium. The interpretation is that as a significant amount of europium is added to the material, substitutional europium-substitutional sodium pairs form which do not reorient thereby eliminating the 163 K peak.

Next, for concentrations above 0.1 mol-% a new peak, which is rather broad, appears at higher temperatures (240 K at 1000 Hz) as a shoulder on the conductivity region. The intensity appears to further increase above the conductivity curve until a concentration of 1.0%. As is apparent in Figure 1, a peak with similar features also is observed for Gd and Dy at high concentrations. It appears that this peak is correlated with the principal ITC peak of Capelletti et al,¹⁰ that occurring at about 152K.

The reason is as follows. In general, ITC peaks in the vicinity of 155 K occur about 87 K lower than the corresponding dielectric relaxation peak at 1000 Hz. For example, the 1000 Hz Type I dipole relaxation in $\text{SrF}_2\text{:La}$ is found at 243 K¹⁵ while the corresponding ITC peak occurs at about 156 K.¹⁶ In $\text{CdF}_2\text{:Eu}$, the principal ITC peak occurs at about 152 K which is 88 K below the value of 240 K reported in Table 1. A more quantitative approach is to calculate the peak position expected for an ITC peak assuming that ITC behaves approximately as a low frequency dielectric relaxation experiment. For example, using the expression $\omega\tau=1$, an angular frequency of 15.7 mr/s accurately describes the position of the ITC peak associated with the Type I dipole in $\text{SrF}_2\text{:La}$. This frequency then predicts a position of 156 K for the principal relaxation in $\text{CdF}_2\text{:Eu}$ which is the same as the observed value to within the uncertainty caused by heating rates, etc. Still another reason for associating the peaks is that they behave similarly upon thermal treatment. Curve (e) in figure 2 shows the spectrum for the 0.5% Eu^{3+} sample which was rapidly cooled to room temperature, after being annealed at 500°C for several hours. Comparison with curve (c) shows that the peak increases significantly with respect to the background conductivity, which is the same behaviour observed for the principal ITC peak.¹⁰ Consequently, the correlation is strongly suggested.

There is also some correlation between the present dielectric results and the site selective spectroscopy studies of Mho and Wright⁶ in Eu^{3+} doped CdF_2 . They find that for low dopant concentrations, essentially only cubic Eu^{3+} sites are found i.e. there is no association between Eu^{3+} and charge compensating F_i^- interstitials. This explains the lack of relaxations observed at low dopant concentrations in the present work.

With increasing doping levels, the cubic site concentration increases until clusters form. This suggests that the origin of the peak at 240 K and 1000 Hz is associated with clusters. In fact, the peak at 240 K exhibits the same concentration and thermal treatment dependence as does the B site of Mho and Wright.⁶ Consequently, this suggests a correlation between the B site and the 240 K dielectric relaxation. On the basis of the above discussion, this suggests a correlation between the principal ITC peak of Capelletti et al.¹⁰ and the B site. This result disagrees with the original identification of the ITC peak as due to a simple dipole¹⁰ as the B site has been identified as due to a cluster.⁶

Next, as shown in figure 3, a monotonic decrease in the magnitude of the electrical conductivity with increasing concentration was observed. A similar decrease in the conductivity at room temperature was also observed for most of the other rare earths and is opposite to the behaviour for CdF_2 doped with alkali metals where the conductivity is enhanced by the increase in the concentration of fluorine vacancies. This unusual behaviour in the conductivity must be reconciled with the increase in concentration of cubic Eu^{3+} sites which is known to occur.⁶ Whatever the conducting species, presumably they either become trapped or their mobility is reduced by the high concentration defect configurations.

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Table 1. Relaxation parameters for several peaks in cadmium fluoride doped with trivalent impurities. The values of T_m are for 1000 Hz.

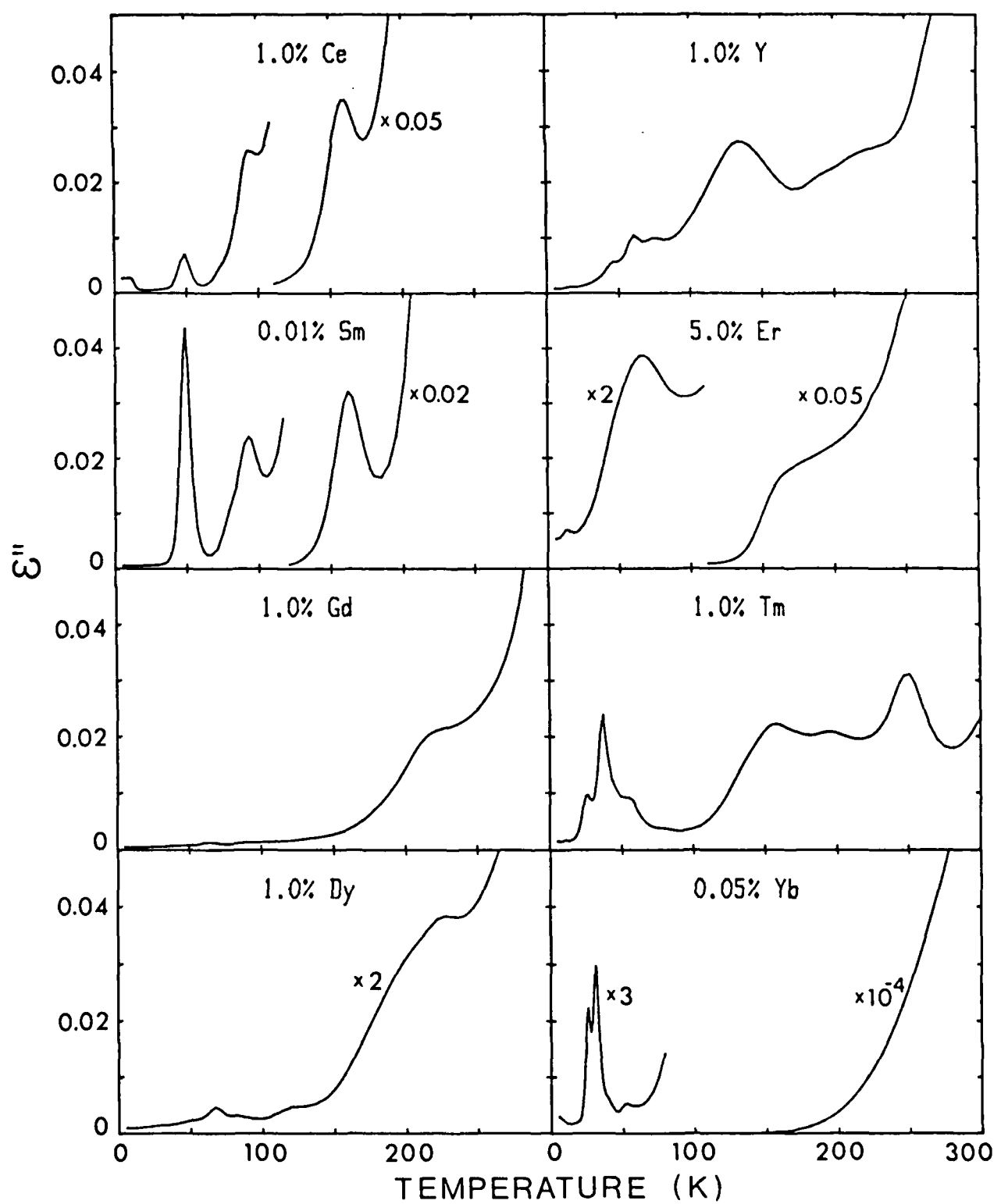
Dopant	T_m (K)	ϵ''_{\max}	h (eV)	τ_0 (10^{-14} s)
1.0 mol-% Ce	48.5	0.0071	0.084	27.4
	94.3	0.0026	0.157	69.4
	159	0.696	0.307	3.11
0.01 mol-% Sm	48.6	0.0436	0.084	34.0
	92.8	0.0239	0.159	36.4
	162.8	1.60	0.315	2.79
0.001 mol-% Eu	162.7	0.0050	0.316	2.56
0.5 mol-% Eu	240	0.005	0.496	0.58
1.0 mol-% Dy	67	0.0023	0.123	9.3
1.0 mol-% Y	61	0.0104	0.104	41.9
	134	0.0274	0.170	7968
	275	0.0533	0.623	0.075
5.0 mol-% Er	67	0.0194	0.147	0.125
1.0 mol-% Tm	157	0.0222	0.245	221
	251	0.031	0.533	0.267

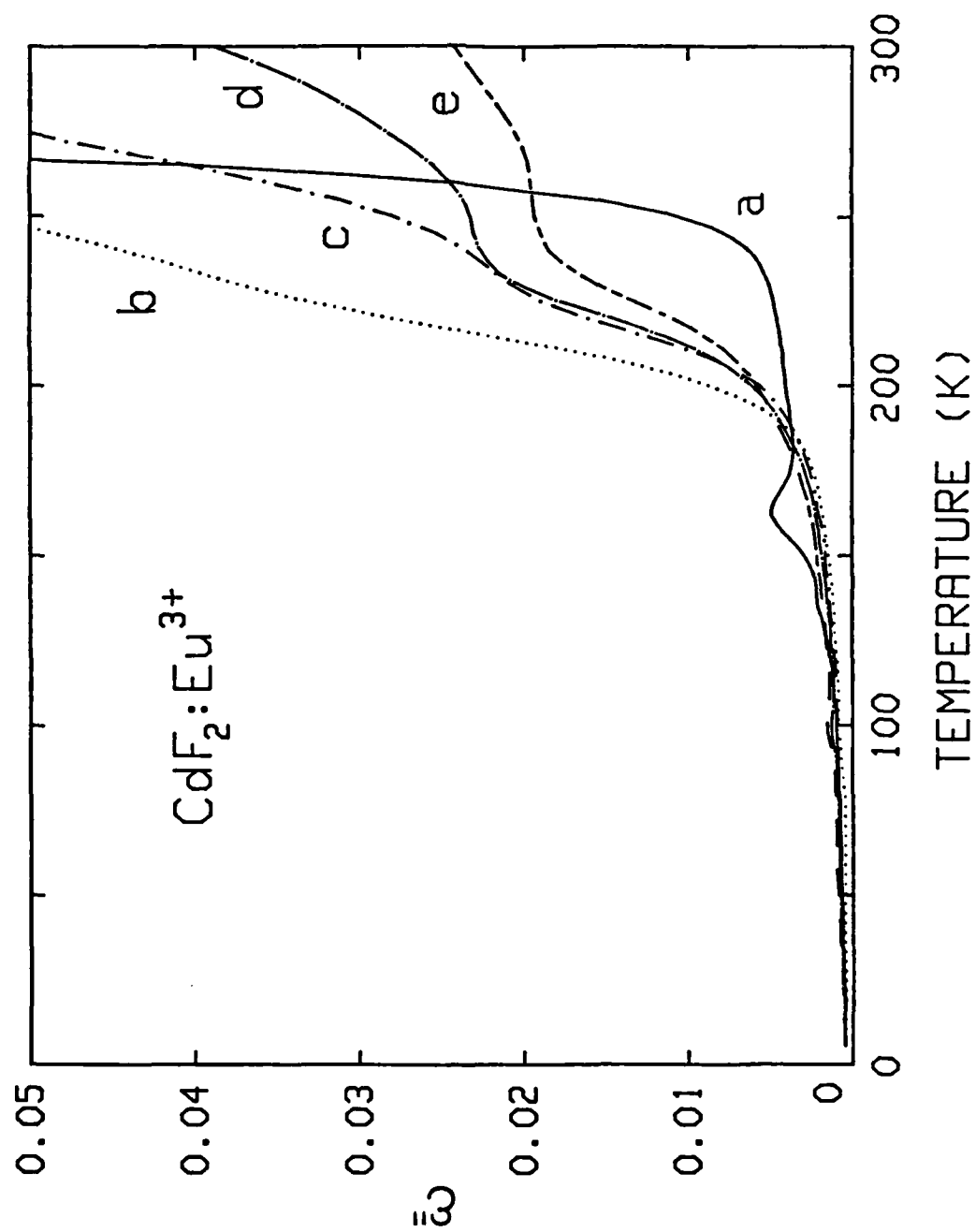
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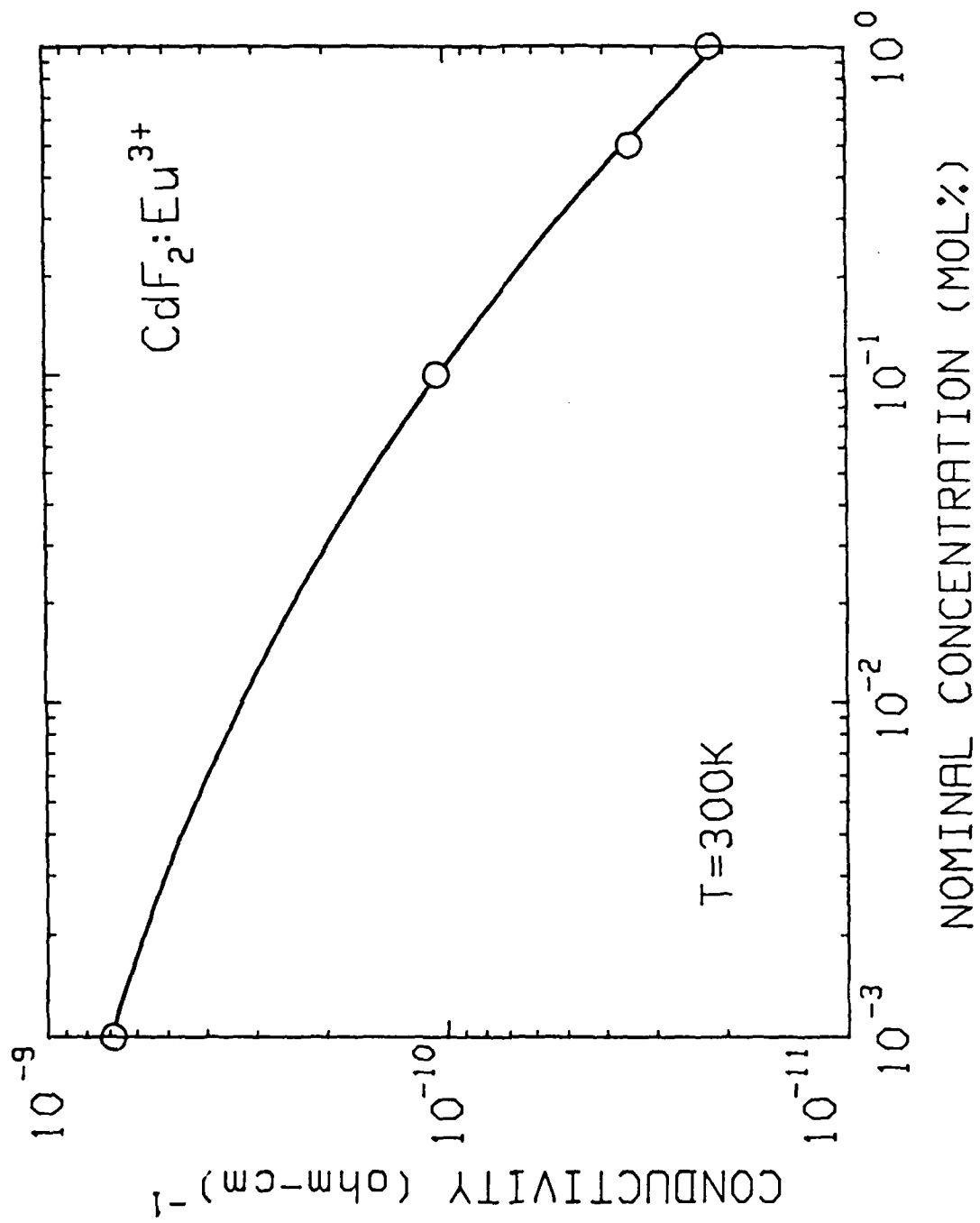
Figure 1. ϵ'' vs. $T(K)$ for various rare earths and yttrium in cadmium fluoride at 1000 Hz. Note that several data sets have been multiplied by the indicated factor.

Figure 2. ϵ'' vs. $T(K)$ for as received crystals of cadmium fluoride doped with the following amounts of europium : (a) 0.001 mol-%, (b) 0.1 mol-%, (c) 0.5 mol-%, and (d) 1.0 mol-%. Curve (e) is for the 0.5 mol-% sample after quenching from 500°C.

Figure 3. Variation of the conductivity of cadmium fluoride doped with europium at room temperature (300K) vs. the nominal molar concentration.







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